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13. ABSTRACT The dependence of the second- and third-order polarizabilities on ground-state polarization was measured for a series of donor-acceptor polyenes using electric field induced second harmonic generation and third harmonic generation, respectively. The changes in ground-state polarization, associated with the donor/acceptor strength or solvent polarity, were probed by x-ray crystallography, nuclear magnetic resonance, electronic absorption and Raman spectroscopies. The observed behavior of the second- and third-order polarizabilities as a function of ground-state polarization agrees well with theoretical predictions. In particular, positive and negative peaks, as well as sign changes, were observed for both the second- and third-order polarizabilities. The dependence's for the second- and third-order polarizabilities are consistent with a derivative relationship between them. In addition, the third-order polarizability of a series of molecules possessing zero bond length alternation was found to be negative, in agreement with predictions based on the relationship between the polarizabilities and ground-state geometry.				
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1. ANNUAL TECHNICAL REPORT

a) A comprehensive list of objectives of the research effort.

The objectives of this work are to obtain an accurate assessment of the limitations of the second hyperpolarizability (γ) for molecules of a given length, to develop design strategies for materials wherein γ has been optimized for a given length and to synthesize molecules with optimized γ . In order to do so, a combined theoretical modeling, synthesis and measurement program has been initiated.

b) Status of the research effort.

Recent studies^{1,2} have suggested that optimizing the polarizabilities of donor-acceptor polyenes requires a specific degree of mixing between neutral and charge-separated resonance structures. The degree of mixing is related to the donor/acceptor strength and can be correlated with the ground-state polarization (i.e. the dipole moment) and a molecular parameter, bond length alternation (BLA), defined as the difference between the average single and double carbon-carbon bond lengths in the polymethine chain. Figure 1 illustrates how chemical modifications can systematically tune the bond length alternation by varying the degree of mixing between neutral and charge-separated structures. For unsubstituted polyenes, or chromophores with weak donors/acceptors, **A**, the ground-state structure resembles that of the neutral resonance form resulting in large positive BLA.³ Increasing the mixing between the two limiting resonance forms by utilizing the stronger dicyanovinyl acceptor, **B**, results in increased ground-state polarization and smaller BLA.³ Complete mixing of the limiting resonance forms results in essentially zero BLA, as for symmetrical cyanines, **C**.⁴ In neutral donor/acceptor systems, increasing the donor and/or acceptor strength further, **D**, results in the charge-separated resonance form being the dominant contributor to the ground state, resulting in negative BLA.⁵

For a particular chromophore, the degree of BLA can be fine-tuned by utilizing solvents of varying polarity since the degree of mixing between neutral and charge-separated resonance structures is known to be sensitive to this perturbation.^{3,6,7} Since polar solvents can stabilize the charge-separated structure to a larger extent than nonpolar solvents, the ground-state polarization of a donor-acceptor molecule can thus be increased by utilizing increasingly polar solvents, since this increases the contribution of the charge-separated form to the ground-state geometry.

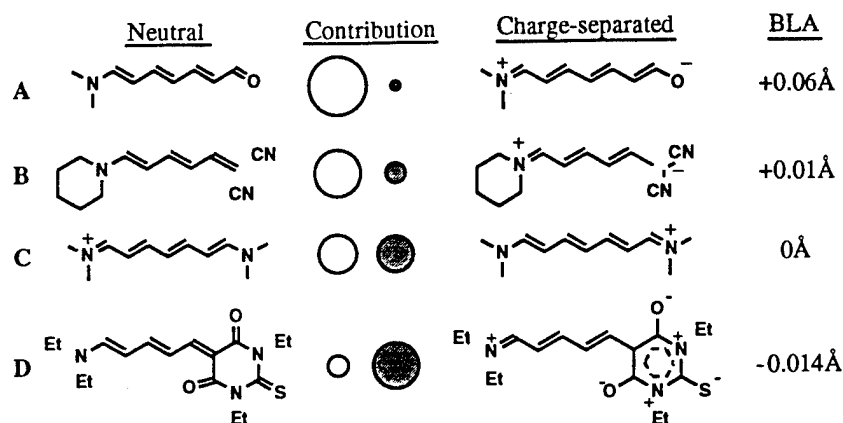


Figure 1. Contribution of neutral and charge-separated resonance forms, given qualitatively by the area of the open and shaded circles respectively, to the ground state. BLA values, tuned by varying donor/acceptor strengths, were determined from x-ray diffraction.³⁻⁵ Et \equiv C₂H₅.

Quantum mechanical calculations have been used to predict the dependence of the polarizability of donor-acceptor molecules on bond length alternation.^{2,8} The predicted correlation of the first-, second- and third-order polarizability (α , β and γ respectively) with bond length alternation is depicted in Figure 2 where it can be seen that: (i) the polarizabilities can be optimized as a function of BLA; (ii) relationships between the various order polarizabilities exist, which are consistent with the n^{th} -order polarizability being related to the derivative of the $(n-1)^{\text{th}}$ -order polarizability. In this paper, the polarizabilities of a series of donor-acceptor polyenes exhibiting a wide range of ground-state polarization were probed to test the structure-property relationships depicted in Figure 2.

THEORETICAL DEPENDENCE OF THE POLARIZABILITIES ON BLA

A detailed explanation of the predicted dependence of the polarizabilities on BLA is presented elsewhere,⁸ but briefly it can be understood by consideration of the behavior of the terms in simplified sum-over-states expressions for α , β and γ , as a function of BLA.

$$\alpha \propto \frac{(\mu_{ge})^2}{E_{ge}} \quad (1)$$

$$\beta \propto \frac{(\mu_{ge})^2 (\mu_{ee} - \mu_{gg})}{(E_{ge})^2} \propto \frac{\alpha (\mu_{ee} - \mu_{gg})}{E_{ge}} \quad (2)$$

$$\gamma \propto \underbrace{-\frac{(\mu_{ge})^4}{(E_{ge})^3}}_{N1} + \underbrace{\frac{(\mu_{ge})^2 (\mu_{ee'})^2}{(E_{ge})^2 E_{ge'}}}_{P1} + \underbrace{\frac{(\mu_{ge})^2 (\mu_{ee}-\mu_{gg})^2}{(E_{ge})^3}}_{P2} \quad (3)$$

where μ and E are the dipole matrix element and transition energy, respectively, between the subscripted states. The subscripts g, e and e' label the ground, first excited and upper excited states respectively.

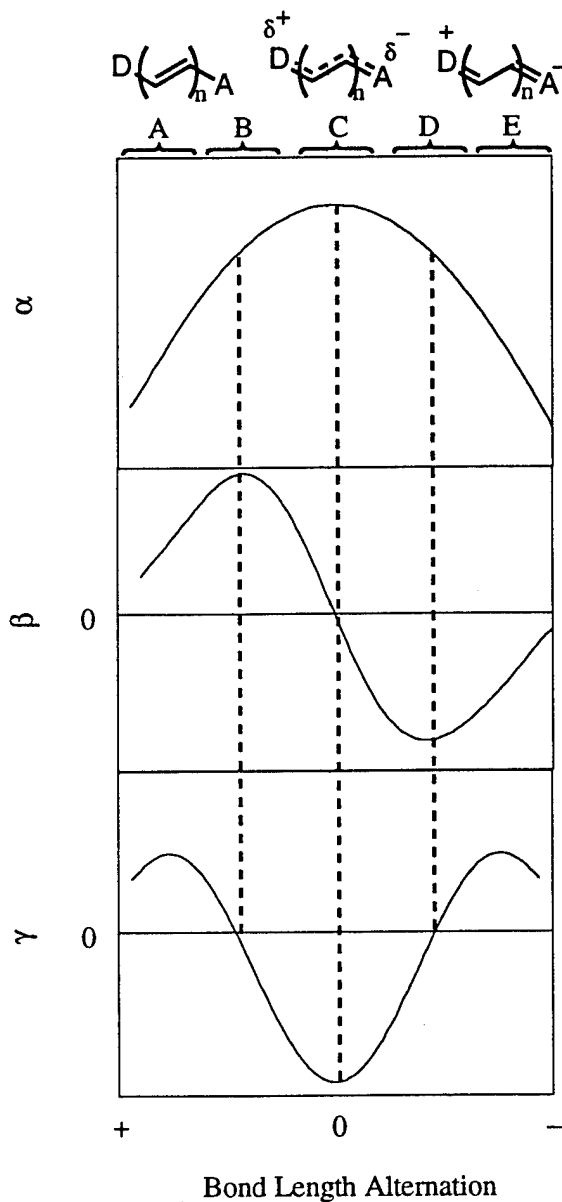


Figure 2. Schematic illustration of the predicted dependence of α , β and γ on bond length alternation. The ground-state polarization increases from A to E.

The first-order polarizability, α , is dependent on two terms, $(1/E_{ge})$ and μ_{ge} , which both peak¹ at the cyanine-limit of zero bond length alternation (Figure 3), explaining the dependence of α on BLA in Figure 2. The two-level model⁹ for β is similar to an α -term scaled by a factor of $(\mu_{ee}-\mu_{gg})/E_{ge}$. The difference in dipole moment between the ground and excited state, $(\mu_{ee}-\mu_{gg})$, exhibits positive and negative peaks at BLA values corresponding to regions A and E respectively (Figure 3).^{1,2,8,10} Thus β , as a function of increasing ground-state polarization, starts positive, increases, peaks in a positive sense, decreases, crosses through zero at the limit of zero BLA, becomes large and negative, peaks in a negative sense and eventually decreases in magnitude (Figure 3).^{1,2,8,10} β displays positive and negative peaks closer to the zero BLA limit (i.e. regions B and D, respectively) than the $(\mu_{ee}-\mu_{gg})$ peaks (Figure 3) since $(1/E_{ge})$ and μ_{ge} peak at the zero BLA limit.

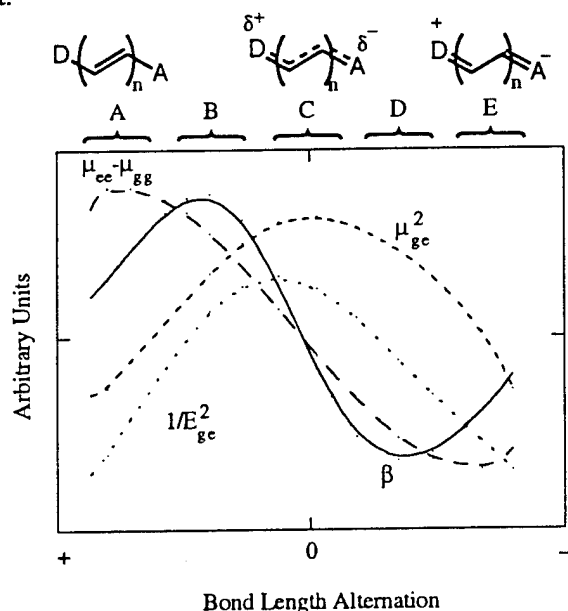


Figure 3. Dependence of $(\mu_{ge})^2$, $(1/E_{ge})^2$, $(\mu_{ee}-\mu_{gg})$ and β on the ground-state structure. The ground-state polarization increases from A to E. The point where $(\mu_{ee}-\mu_{gg})$ and β are zero corresponds to the bond-equivalent cyanine-limit of zero bond length alternation. The curves were calculated⁸ for $\text{Me}_2\text{N}-(\text{CH}=\text{CH})_4\text{-CHO}$, geometry-optimized in the presence of a static electric field (used to modify the geometry from the highly bond-alternate polyene-limit (region A), through the bond-equivalent cyanine-limit (region C) to the bond-alternate charge-separated polyene-limit (region E)), at the semiempirical INDO level using a sum-over-states approach in combination with an INDO-configuration interaction technique that includes full single and limited double configuration excitations.

The three-level model¹¹⁻¹³ for the third-order polarizability, γ , consists of a negative, α^2 -like term, N1, a two-photon term, P1, and a β -like term, P2. For chromophores with large positive BLA, such as unsubstituted polyenes, the P2 term is negligible due to small $(\mu_{ee}-\mu_{gg})$ and the P1 term dominates N1 resulting in positive γ (Figure 2).^{7,11} By increasing the ground-state polarization and thus decreasing BLA, the P2 term, like β (Figures 2 and 3), starts to increase and hence γ increases. However, increasing the ground-state polarization toward the cyanine-limit (region C) also increases $|N1|$ and therefore a positive peak in the γ curve is evident at larger magnitudes of BLA than the peak in the β -like P2 term. Upon further polarization, P2 peaks in a positive sense and starts to decrease and $|N1|$ continues to increase and thus γ decreases in magnitude until $|N1| = P1 + P2$ and γ is zero.^{7,8} At the bond-equivalent cyanine-limit (region C), the P2 term is zero since $(\mu_{ee}-\mu_{gg})$ is zero. The γ curve exhibits a negative peak at this point since both $|N1|$ and P1 peak but $|N1| > |P1|$.^{7,8} To a first approximation, the behavior of γ in the region of negative BLA mirrors that in the positive BLA region (Figure 2).

The observation that α , β and γ appear to be related by a derivative-like relationship can be understood by considering a Taylor series expansion of the dipole moment,

$$\mu = \mu_0 + \alpha E + \frac{1}{2}\beta E^2 + \frac{1}{6}\gamma E^3 + \dots \quad (4)$$

where

$$\alpha = \left. \frac{\partial \mu}{\partial E} \right|_0 \quad \beta = \left. \frac{\partial^2 \mu}{\partial E^2} \right|_0 \quad \gamma = \left. \frac{\partial^3 \mu}{\partial E^3} \right|_0 \quad (5)$$

so that

$$\beta = \left. \frac{\partial \alpha}{\partial E} \right|_0 \quad \gamma = \left. \frac{\partial \beta}{\partial E} \right|_0 \quad (6)$$

Now if we consider a molecule to be polarized by a strong field, F , that can modify the degree of bond length alternation associated with the molecule, the dipole moment will depend on F in some characteristic way,

$$\mu = \mu(F) \quad (7)$$

for which a single Taylor series with constant coefficients is not a sufficient description. Qualitatively, we would expect, and AM-1,² INDO⁸ and valence bond calculations¹⁴ show: (i)

that for weak fields, such that the BLA is polyene-like, μ will be small and weakly dependent on field; (ii) that when the field is large, such that the structure is close to the bond-alternate charge-separated polyene-limit, μ will be large and weakly dependent on field; (iii) that for moderate fields, μ will be intermediate and will vary most rapidly with field, i.e. the rate of change of the BLA with field is largest at the cyanine-limit.

At any particular value of F , say F' , we can expand μ in a Taylor series, and thus

$$\alpha = \left. \frac{\partial \mu}{\partial F} \right|_{F'} \quad \beta = \left. \frac{\partial \alpha}{\partial F} \right|_{F'} \quad \gamma = \left. \frac{\partial \beta}{\partial F} \right|_{F'} \quad (8)$$

Therefore the functions $\alpha(F)$, $\beta(F)$ and $\gamma(F)$ will be given by

$$\alpha(F) = \frac{\partial \mu(F)}{\partial F} \quad \beta(F) = \frac{\partial \alpha(F)}{\partial F} \quad \gamma(F) = \frac{\partial \beta(F)}{\partial F} \quad (9)$$

leading to derivative relationships between a given polarizability and the lower-order polarizability. Keeping in mind that the ground-state polarization, and hence BLA, is a function of the field strength, i.e. $BLA = BLA(F)$, that if we want to map the polarizabilities as a function of BLA, that the change of variables is nonlinear, i.e.

$$\alpha = \frac{\partial \mu}{\partial F} \frac{\partial F}{\partial BLA} \quad (10)$$

since BLA is a nonlinear function of F . This leads to a change of the shape of the α , β and γ curves versus BLA compared to those versus F . Nonetheless, the relation of the peaks and zero crossings of the different polarizabilities, e.g. the peak of α and the zero crossing of β , are preserved and we will use these special points to test experimentally the validity of these relationships.

MODEL COMPOUNDS AND DEGREES OF BLA

The molecules (Figure 4) studied to test the predicted structure-property relationships were chosen since strong evidence exists that they approximately cover the BLA range A-E in Figure 2.¹⁰ The bond length alternation values were coarsely changed by utilizing donors and acceptors

of varying strength and fine-tuned using solvent polarity. Bond length alternations, determined from x-ray crystallography, of unsubstituted polyenes and **3**, containing the weak formyl acceptor, have been reported previously^{3,15} and allow an assignment of **1-3** to region A. This assignment is consistent with the positive solvatochromism displayed by **3** in all solvents used (Table I).

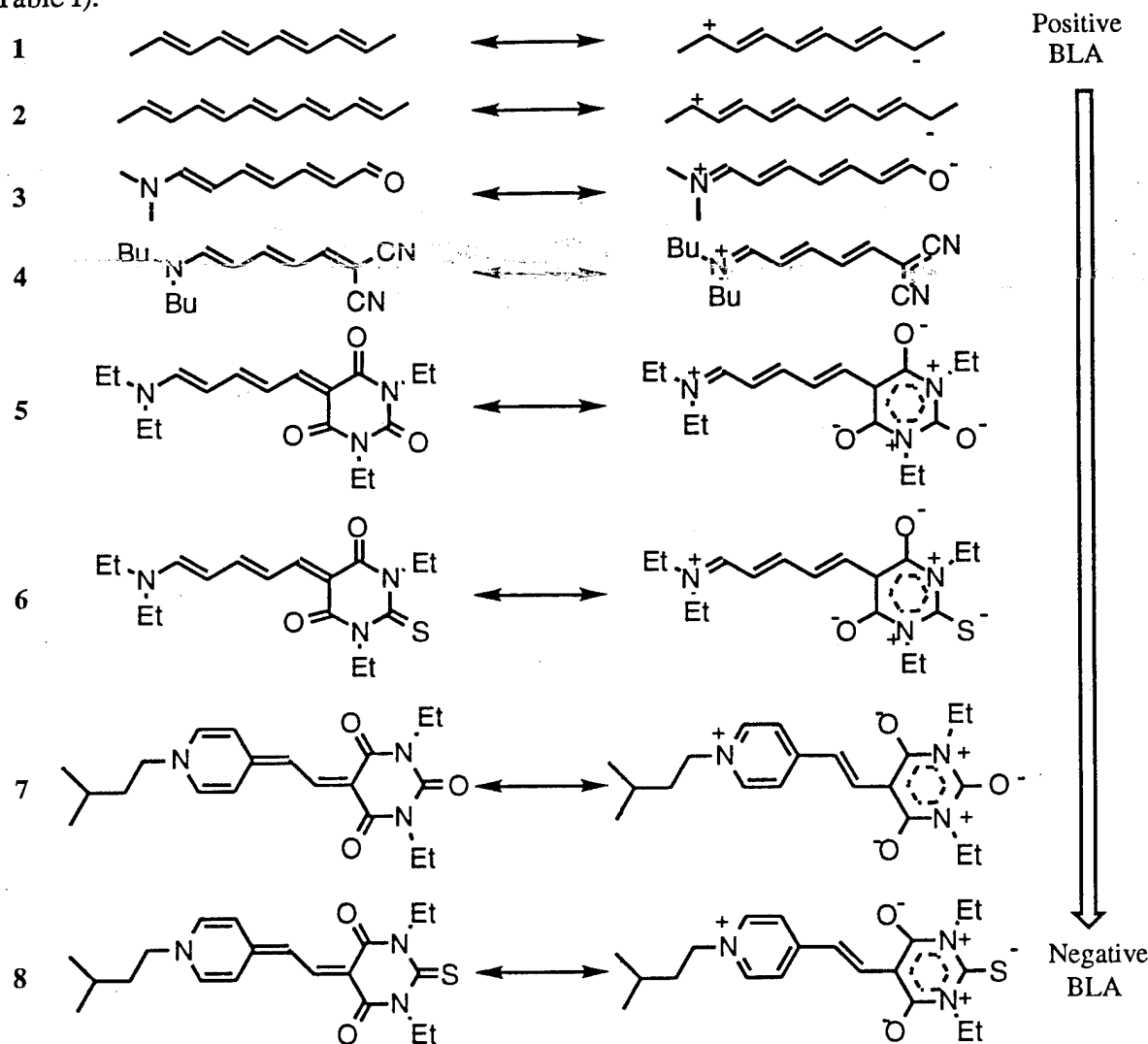


Figure 4. Canonical resonance structures for the donor-acceptor polyenes investigated. Electron donor/acceptor strength increases from **3** to **8**. Et \equiv C₂H₅ and Bu \equiv n-C₄H₉.

Compound **4** with the stronger dicyanovinyl acceptor possesses a bond length alternation of $+0.015\text{\AA}$ in the solid state, assigning this molecule to region B. Interestingly, this small BLA value suggests that in polar solvents the ground-state geometry is cyanine-like whereas in

nonpolar solvents, due to a decreased contribution of the charge-separated state, the ground-state structure is more similar to an unsubstituted polyene. These solvent-dependent geometry changes on a related molecule (**B**, Figure 1) were probed by non-resonant Raman spectroscopy (Figure 5).³ The Raman spectrum of the unsubstituted polyene, (Figure 5a), exhibits two main bands, those due to the C–C (1150 cm^{-1}) and C=C modes (1600 cm^{-1}). The Raman spectrum of the bond-equivalent cyanine, (Figure 5d), exhibits increased activity at intermediate frequencies consistent with the loss of discrete C–C and C=C character. As predicted, the Raman spectrum of the dicyanovinyl moiety in nonpolar solvents (CHCl_3 , Figure 5b) is qualitatively similar to that of the polyene whereas the spectrum in polar solvents (CH_3CN , Figure 5c) is qualitatively similar to that of the cyanine. The positive solvatochromism displayed by **4** in all solvents used (Table I) is consistent with the structural assignment of region B.

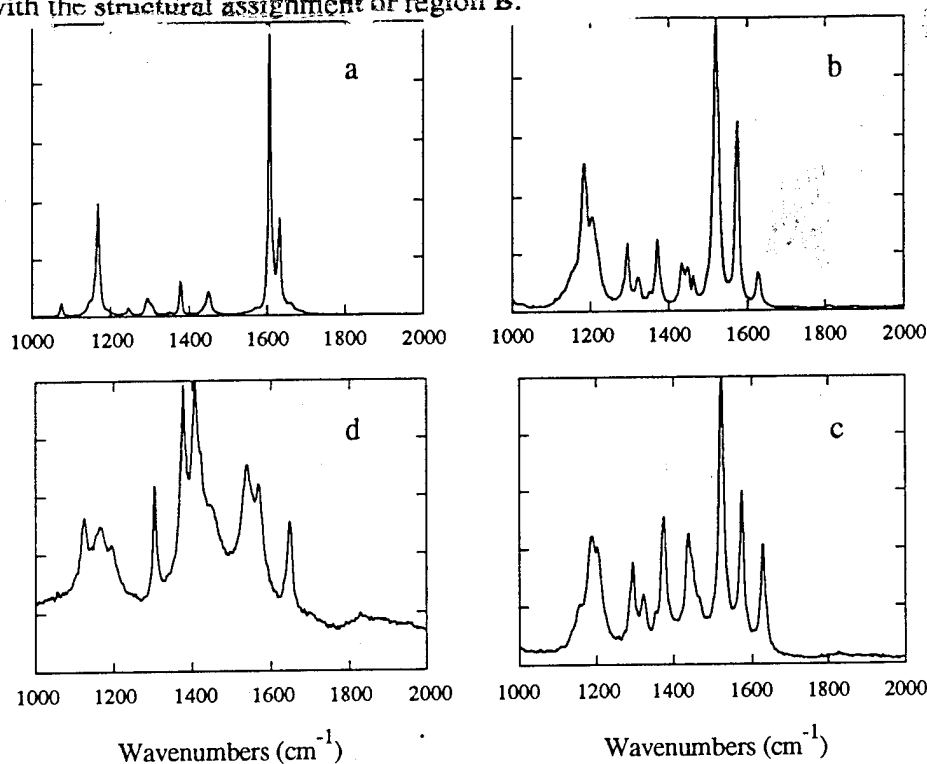


Figure 5. Raman spectra for (a) The polyene deca-tetraene (**1**, Figure 4) in the solid state; (b) **B** (Figure 1) in CHCl_3 ; (c) **B** (Figure 1) in CH_3CN ; (d) A cyanine (**C**, Figure 1), in CH_3CN .³ The counterion for the cyanine was perchlorate.

The ground-state polarization can be increased (bond length alternation decreased) further by utilizing the barbituric and thiobarbituric acid acceptors, **5** and **6** respectively. In fact, BLA for **6** in the solid state is -0.014 \AA (Figure 1), which indicates that the ground-state geometry is biased slightly towards the charge-separated canonical resonance form. Both **5** and **6** display positive

solvatochromism in nonpolar solvents, whereas negative solvatochromism is displayed for **5** in highly polar solvents and **6** in moderate polarity solvents, consistent with **5** being in region B/C and **6** in region C.

Molecules **7** and **8** display negative solvatochromism in all solvents used. Furthermore, the large ^1H - ^1H coupling constants (Figure 6) across the central carbon-carbon bond are consistent with a trans double bond (as depicted in the zwitterionic form in Figure 4, right) assigning **7** and **8** to regions C/D and D/E respectively. These coupling constants increase with increasing solvent polarity, consistent with an evolution of the ground-state geometry towards a more charge-separated structure.

The product of the ground-state dipole moment, μ , and the second-order polarizability, β , was determined by solvent-dependent, electric field induced second harmonic generation (EFISH) measurements at 1907 nm using apparatus and methodology described elsewhere.¹⁷ The third-order polarizability, γ , was determined by solvent-dependent third harmonic generation (THG) measurements at 1907 nm. A description of the experimental apparatus and data reduction scheme has been reported previously.¹⁸

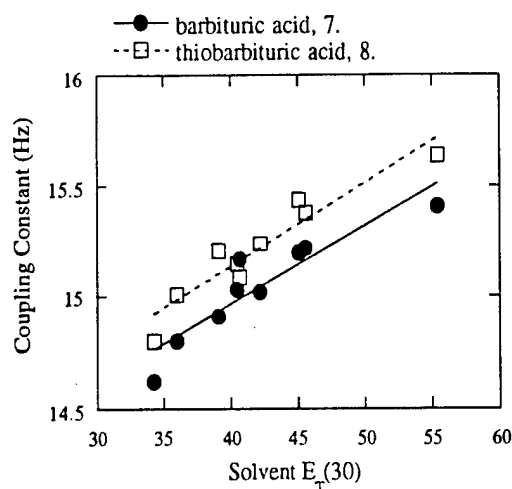


Figure 6. The ^1H - ^1H coupling constants for **7** and **8** as a function of solvent polarity.¹⁶ The trend of increasing coupling constant with increasing solvent polarity is indicative of an evolution towards a more charge-separated ground state (Figure 4, right).

RESULTS AND DISCUSSION

The solvent-dependent polarizabilities for the molecules in Figure 4 are presented in Table I. Molecules **1** and **2** display positive γ values consistent with those expected given the large positive bond length alternation values from previous structure determinations.¹⁵ The increase of γ with increasing conjugation length has been noted by other authors.¹⁹ Molecule **3**, with the weak formyl acceptor, displays an increasing $\mu\cdot\beta$ product and a positive peak in γ with increasing solvent polarity. This behavior is consistent with that expected for the structural assignment above **3** in region A (Figure 2). The increase in γ for the donor-acceptor polyene, **3**, over that of the symmetrical unsubstituted polyenes **1** and **2** has been noted previously¹¹ and is due to the lowering of symmetry with the result that the P2 term (equation 3) contributes positively to γ .

Compound **4** with the stronger dicyanovinyl moiety displays a positive peak in $\mu\cdot\beta$ and a sign change in γ . In fact, the $\mu\cdot\beta$ peak and the zero crossing of γ occur simultaneously, consistent with the derivative-like relationship predicted in Figure 2 and with the structural assignment of **4** in region B.

Molecules **5** and **6** display decreasing $\mu\cdot\beta$ products with increasing solvent polarity. For **5** in the most polar solvent and for **6** in moderate polarity solvents, $\mu\cdot\beta$ changes sign, consistent with the ground-state geometry being tuned through the cyanine-limit of zero bond length alternation. The γ values for **5** become large and negative with increasing solvent polarity with some evidence that γ peaks in a negative sense in the most polar solvents. Molecule **6** displays a clear negative γ peak in moderate polarity solvents. The zero crossing of the $\mu\cdot\beta$ curve for both **5** and **6** coincides with the negative γ peak, consistent with the proposed structure-property relationships. Additionally, to the extent to which α can be represented by $(1/E_{ge})$, α is maximized at the zero crossing of $\mu\cdot\beta$, again consistent with the predicted trend (Figure 2).

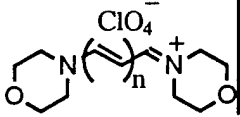
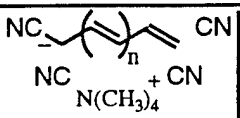
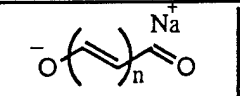
By increasing the ground-state polarization further, as with molecules **7** and **8**, there is some evidence that the degree of mixing required to maximize $\mu\cdot\beta$ in a negative sense has been achieved.¹⁰ A zero-crossing in γ for **7** in nonpolar solvents is observed as well as evidence of γ approaching a positive peak for **8** in the most polar solvents. The zero crossing of γ however does not coincide with the negative peak in $\mu\cdot\beta$. This may be explained by the large ground-state dipole moment shifting the peak in $\mu\cdot\beta$ to lie closer to the γ peak than would the β peak.

Table I. Maximum absorption wavelength (λ_{\max} , units of nm), solvent-dependent $\mu\beta$ (units of 10^{-48} esu) and γ (units of 10^{-36} esu) for 1-8. The estimated precision in $\mu\beta$ and γ is $\pm 15\%$. The polarity of the solvents increase (the contribution of the charge-separated structure to the ground-state geometry increases) from left to right. Normalized $E_T(30)$ values¹⁶ of the solvents are presented within parentheses.

Molecule	Solvent								Region
	CCl ₄ (0.052)	C ₆ H ₆ (0.111)	1,4-Dioxane (0.164)	CHCl ₃ (0.259)	CH ₂ Cl ₂ (0.309)	CH ₃ CN (0.456)	CH ₃ NO ₂ (0.482)	CH ₃ OH (0.762)	
1									
λ_{\max}	-	300	300	-	300	-	-	-	A
$\mu\beta$	-	-	-	-	-	-	-	-	
γ	-	34	25	-	27	-	-	-	
2									
λ_{\max}	-	328	350	-	330	-	-	-	A
$\mu\beta$	-	-	-	-	-	-	-	-	
γ	-	60	70	-	72	-	-	-	
3									
λ_{\max}	396	404	402	420	420	418	426	440	A
$\mu\beta$	299	272	-	322	343	348	430	-	
γ	-	-	40	95	105	113	113	73	
4									
λ_{\max}	446	472	468	478	480	476	480	476	B
$\mu\beta$	332	360	-	400	340	231	195	-	
γ	40	15	-25	-42	-50	-120	-117	-135	
5									
λ_{\max}	498	504	502	510	508	502	506	500	B/C
$\mu\beta$	401	205	-	200	141	109	-65	-	
γ	-	-20	-100	-135	-145	-205	-220	-166	
6									
λ_{\max}	526	532	528	536	534	524	526	520	C
$\mu\beta$	276	264	-	-22	-60	-240	-316	-	
γ	-	-85	-170	-195	-175	-130	-125	-10	
7									
λ_{\max}	528	520	510	510	506	488	490	468	C/D
$\mu\beta$	-	-180	-	-374	-414	-	-350	-	
γ	-	-	-25	15	30	79	73	150	
8									
λ_{\max}	548	538	526	526	520	496	496	482	D/E
$\mu\beta$	-	-	-	-600	-770	-550	-363	-	
γ	-	-	-	130	167	228	227	291	

The structure-property relationships proposed in Figure 2 can be further tested by examining the third-order polarizability of molecules possessing zero bond length alternation, for example cyanines and oxonols. The results for a series of these chromophores are presented in Table II where it can be seen that, with the exception of the shortest chromophores, the γ values are negative as predicted.

Table II. γ values (units of 10^{-36} esu) and maximum absorption wavelengths (λ_{\max} , units of nm) for molecules possessing zero bond length alternation. The estimated precision in γ is $\pm 15\%$, except in the case where the magnitude of $\gamma < 3 \times 10^{-36}$ esu when the estimated error in γ is $\pm 5 \times 10^{-36}$ esu.

Molecule	n	λ_{\max}	γ
	1	318	+ 3
	2	416	- 40
	3	516	- 370
	1	438	- 45
	2	538	- 500
	1	266	+ 3
	2	362	- 7

SUMMARY

Donor-acceptor polyenes of comparable conjugation length have been synthesized and their solvent-dependent hyperpolarizabilities probed by EFISH and THG measurements at 1907 nm. Optimization in both a positive and negative sense, as well as sign changes in $\mu \cdot \beta$ and γ were observed. These observations were explained by molecular structure changes (probed by x-ray crystallography, $^1\text{H-NMR}$, electronic absorption and Raman spectroscopies) resulting from the variation of mixing of neutral and charge-separated resonance forms upon changing the donor/acceptor strengths and solvent polarity. The trend of the geometry-dependent hyperpolarizabilities is fully consistent with the trends predicted using geometry-optimized electric-field-dependent AM1 and INDO-CI calculations and with the prediction that the polarizabilities are related by a derivative relationship. A separate series of ionic molecules

possessing zero bond length alternation were found to exhibit negative third-order polarizabilities, also in agreement with the proposed structure-property relationships.

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The Effect of Molecular Polarization on Bond Length Alternation, Linear Polarizability, First and Second Hyperpolarizability in Donor-Acceptor Polyenes as a Function of Chain Length

Introduction

Donor-acceptor polyenes are the prototypical organic chromophores that have been considered for their nonlinear optical (NLO) response. In attempting to understand the relationship between chemical structure and the linear and nonlinear optical properties of molecules, two relevant molecular parameters are typically varied: ground-state polarization (by varying the relative strengths of the donor and acceptor), and the molecular length. We have recently described a procedure that permits us to calculate α , β and γ of donor-acceptor polyenes of the form $R_2N-(CH=CH)_n-CHO$ (1) through a range of bond length alternation (BLA) corresponding to differing degrees of charge-separation in the molecule (Figure 2, shown here for $n=5$ and previously reported for $n=4$).^{1,2} Using this method, the molecule can be varied from a gas-phase form with little charge separation [the polyene limit] depicted by the resonance form on the left side of Figure 1, through a bond length equivalent form in which both resonance forms make an approximately equal contribution [the cyanine limit], through a strongly charge-separated form [the zwitterionic limit] dominated by the resonance structure at the right side of Figure 1. Having established the basic validity of this approach, we now present results of a computational study that varies both BLA and molecular length. We point out that a physically accessible parameter, BLA, can be related to maxima and minima in the molecule's linear polarizability (α), and first- (β) and second molecular hyperpolarizability (γ) for molecules of differing length. In addition, we provide a more detailed description of the computational technique as well as several tests to help validate the procedure.

Results and Discussion

Using the semi-empirical AM1 parameterization in the MOPAC package,^{3,4} we examined donor-acceptor polyenes of the form 1 ($R = Me$, $n = 2-7$) under the influence of an external perturbation designed to vary the ground-state polarization and geometry. This perturbation was two positive and two negative point charges placed as is shown in Figure 1 and moved incrementally towards the molecules (from 40 Å to 4 Å). While the distances between the point charges and the molecule were held fixed, the molecular geometry was optimized. As the point charges were placed closer to the molecules, it was observed that the single bonds in the molecules became shorter (from ≈ 1.44 Å to ≈ 1.35 Å) and the double bonds became longer (from ≈ 1.35 Å to ≈ 1.44 Å). Although this entire range of bond lengths could not be spanned

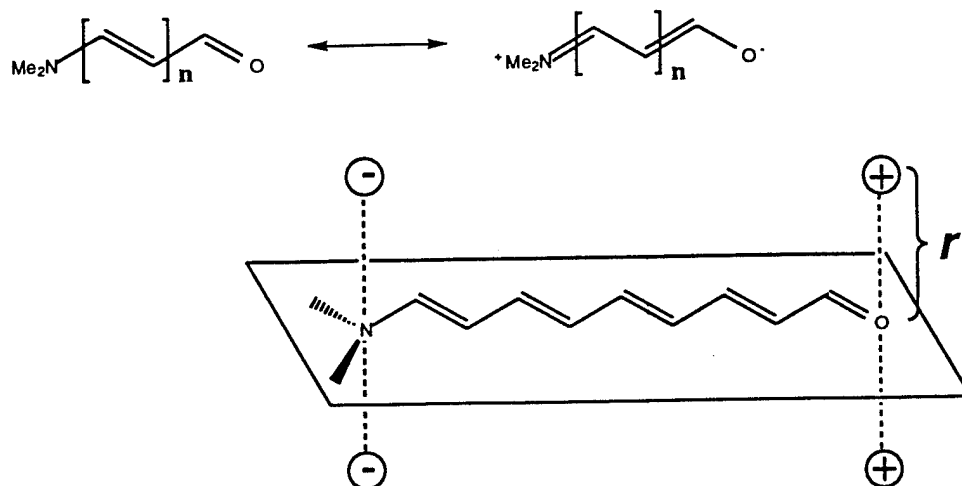


Figure 1. The neutral (top, left) and charge-separated (top, right) resonance structures that contribute to both the electronic and nuclear structure of the molecule and a depiction of the placement of the point charges (bottom). In the absence of an external perturbation, a computational geometry optimization is biased against charge separation and depicts the molecule almost solely as it is represented on the left. Point charges promote increased charge-separated character as they approach the molecule.

for the shorter polyenes under study ($n < 4$), the range corresponds to a change in bond length alternation (defined as the difference between the average of the central $n-2$ C=C bonds and the average of the central $n-2$ C-C bonds in the molecules with the resonance structure shown at the left of Figure 1) from $\text{BLA} \approx -0.09 \text{ \AA}$, represented predominantly by the charge-neutral (left) resonance structure in Figure 1 to $\text{BLA} \approx +0.09 \text{ \AA}$, represented predominantly by the charge-separated (right) resonance structure in Figure 1. At the same time, the ground-state dipole moments of the molecules increased smoothly.

Values for α , β and γ for the polarized molecules were then calculated using a finite field subroutine.⁵ Although polarization by point charges is different than charge stabilization by solvent (in particular, the largest fields applied in our calculations are considerably larger than the reaction fields for common solvents), this method qualitatively reproduces experimental trends in geometry and polarizabilities as a function of increasing ground-state polarization.^{1, 2, 6-10} Several observations are made from Figure 2. (i) The value of α exhibits a peak at the cyanine limit. (ii) The value of β exhibits a positive peak between the polyene and the cyanine limits, crosses through zero at roughly the cyanine limit (at which point the difference between the dipole moment of the strongly allowed first excited state and the ground state is roughly zero²²), and

exhibits a negative peak between the cyanine and zwitterionic limits. (iii) Between the polyene and cyanine limits, the value of γ is initially positive and increases, reaching a peak. The value of γ then decreases, crosses through zero (at a BLA corresponding to that where β peaks), becomes negative, reaching a negative peak (with a maximized absolute value) at the cyanine limit. To first approximation, the region between the cyanine and zwitterionic limits mirrors that on the other half of the curve. (iv) The curves are roughly derivatives with respect to each other as is discussed in detail elsewhere.¹¹ For β and γ , solvent dependent electric field-induced second harmonic generation (EFISH) and third harmonic generation (THG) studies on a series of molecules of similar length and with ground-state polarizations that span almost the entire range of BLA depicted by these curves confirm the behavior predicted in Figure 2.^{8, 12} Furthermore, it has recently been shown that molecules with reduced BLA similar to that at the positive peak in the β curve have exceptionally high nonlinearities.¹³ As discussed earlier,^{1, 2, 6} all of these results are consistent with simplified perturbative expressions which approximate α , β , and γ based upon couplings, transition energies, and changes in dipole moments between the ground and one or two excited states of the molecule.^{6, 14-21} In addition, recent, similar computational studies using a sum-on-states approach,²² using an anharmonic oscillator model,²³ and using a simplified two level valence bond approach²⁴ predict essentially the same relationships as a function of ground-state polarization.

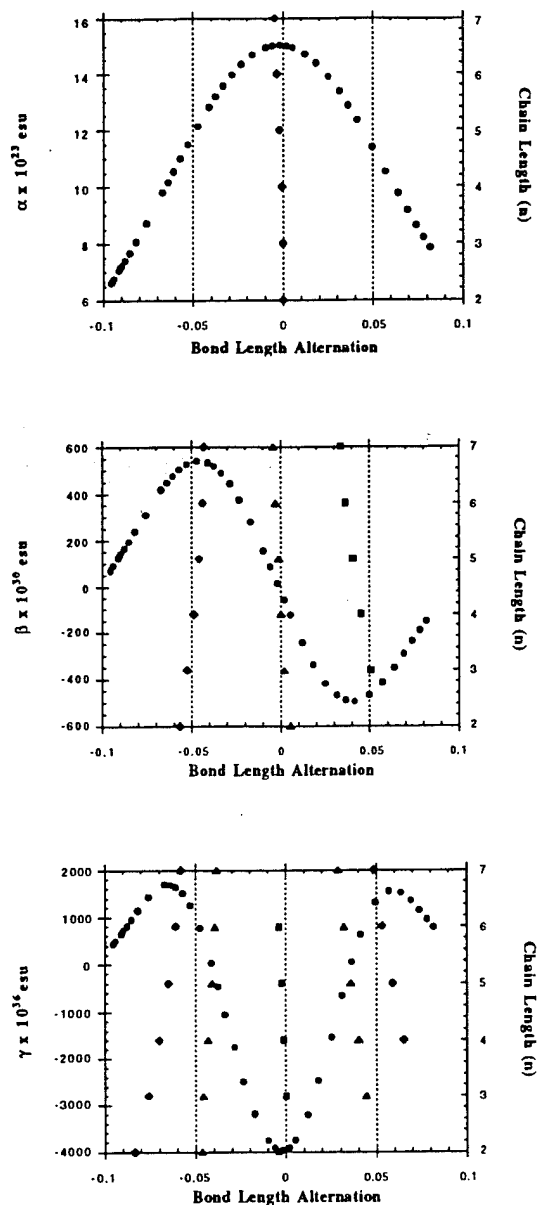


Figure 2. Correlation of molecular polarizability, α (top plot), first, β (center plot) and second, γ (bottom plot) hyperpolarizabilities (on the left axes), with bond length alternation (BLA, defined in the text) for $\text{Me}_2\text{N}-(\text{CH}=\text{CH})_5\text{-CHO}$ (\bullet). The bond length alternation at which α , (top plot), β (center plot) and γ (bottom plot) are maximized (\blacklozenge), are minimized (\blacksquare) or cross through zero (\blacktriangle) for a given of chain-length (n), where n is shown on the right axes. The shorter molecules could not be driven to the most charge separated form ($\text{BLA} > \approx +0.025$), so not all maxima/minima could be reported. Likewise, the 7-double bond polyene could not be driven smoothly through the region of $\text{BLA} = 0$.

When evaluating the molecular length dependence of β , it is common to fit data to a function of the form $\beta(0) \propto N^m$.²⁵⁻²⁸ Here, N is defined as the number of conjugated multiple bonds in the molecule (including the C=O bond, i.e. $N = n + 1$) so as to more accurately represent the real length of the molecule. The exponent, m , lends insight into the chain length dependence of β . We have computed m for β for the molecules at various bond length alternations and for molecules at β_{\max} (Table 1). The exponent m is also computed for α and γ . Exponents derived from data in the literature are also reported (for these cases N is defined as above and therefore exponents may differ from those reported in the original work, due to the use of alternative counting scheme for the conjugation length).²⁹ The exact bond length alternation corresponding to a maximized β and γ varies somewhat with molecular length, and this value is graphically displayed as a function of chain length, n , in Figure 2. It is not expected that each member of this homologous series of molecules will have the same bond length alternation in a given solvent, but the range of exponents, for both constant bond length alternation and for bond length alternation corresponding to a maximized β or γ gives a range into which optimized molecules are expected to fall. In particular, it is expected that increasingly strong donors and acceptors will be required to reach a given BLA value as molecules become longer reflecting the greater difficulty in separating charge over greater lengths. The exponents at or near the maxima or minima of the α s, β , and γ , curves are larger than those computed for hyperpolarizabilities based upon bond length alternate (gas-phase) geometries,^{27, 28} and, in the case of β , for those observed for molecules containing aromatic endgroups.^{7, 30-32} For α , the data shows that chromophores with minimal bond length alternation (the cyanines) are optimized, a conclusion consistent with previous experimental determinations.³³ β is optimized at $\text{BLA} = -0.05 \pm 0.01$ Å, and around this point, $m \approx 4.5$. We have synthesized simple donor-acceptor polyenes such as **1** ($n = 0-3$) as well as $\text{R}_2\text{N}-(\text{CH}=\text{CH})_n-\text{CHC}(\text{CN})_2$, **2** ($n=0-3$) and find that the value for m for these molecules (measured by EFISH in CHCl_3) is 3.2 and 5.4, respectively.³⁴ As mentioned earlier, a series of vinylogous compounds (such as **2**) will not necessarily have the same BLA at different chain lengths. Therefore, it is possible to move closer to the maxima of the curve with increasing chain length, if BLA for a short compound in the series is too close to zero to optimize β and if $|\text{BLA}|$ becomes larger with increasing length. This would result in higher exponents than would be predicted for any given bond length alternation. Conversely, if the magnitude of BLA is greater than that required to optimize β in a positive sense, then for a given donor or acceptor, the exponent is expected to be lower than might be predicted based on short compounds within the series. The magnitude of γ is maximized in the cyanine limit, but also shows a maximum at $\text{BLA} = -0.07 \pm 0.01$ Å which may correspond to more stable molecules, particularly for longer chain lengths. The exponents

corresponding to these extrema are again significantly greater than those predicted previously for polyenes.^{25, 26}

Table 1. Summary of exponents for α , β , and γ of polyenes and polarized polyenes

Quantity	Geometry	m	N's Used	Compounds/Method ^b
α	BLA = -0.09	1.33	3-8	This work
	Maximum ^a	2.16	3-8	This work
	Computational	1.38	3-8	H-(CH=CH) _n -H, N = n using the
	Reference ²⁵			6-31G + PD basis set w. SOS
	Computational	1.31	3-8	H-(CH=CH) _n -H, N = n using
	Reference ²⁶			AM1/FF
β	BLA = -0.09	2.95	3-8	This work
	Maximum ^a	4.51	3-8	This work
	BLA = -0.06	4.28	3-8	This work
	BLA = -0.05	4.49	3-8	This work
	BLA = -0.04	4.61	3-8	This work
	Computational	3.43	3-7	Me ₂ N-(CH=CH) _n -NO ₂
	Reference ²⁷			N = n + 1 using CNDOVSB/SOS
	Computational	3.21 ^c	3,5,7,9	Me ₂ N-(CH=CH) _n -CHO
	Reference ²⁷			N = n + 1 using CNDOVSB/SOS
	Computational	3.52	3-6	Me ₂ N-(CH=CH) _n -NO ₂ ,
	Reference ²⁸			N = n + 1 using PPP/SOS
	Experimental	4.02	4-6	Me ₂ N-Ph-(CH=CH) _n -
	Reference ³²			CH=C(CN) ₂ , N=n+4, EFISH at
				1.06 μ m in chloroform.
	Experimental	2.27	6-9	Me ₂ N-Ph-(CH=CH) _n -Ph-NO ₂ ,
	Reference ³²			N=n+5, EFISH at 1.06 μ m in
				chloroform.

	Experimental Reference ³⁹	2.48	5,8,10,12	$\mu\beta(0)$ values, Julolidine- (CH=CH) _n -CH=C(CN) ₂ , N=n+4, EFISH at 1.91 μ m in chloroform or acetone.
	Experimental Reference ³⁹	3.26	2,5,7,9	$\mu\beta(0)$ values, Benzodithia- (CH=CH) _n -CHO, N=n+1, EFISH at 1.34 μ m in chloroform or acetone.
	Experimental Reference ⁷	3.2	1-4	Me ₂ N-(CH=CH) _n -CHO, N=n+4, EFISH at 1.91 μ m in chloroform
	Experimental Reference ⁷	5.4	2-5	Me ₂ N-(CH=CH) _n -CH=C(CN) ₂ , N=n+2, EFISH at 1.91 μ m in chloroform
γ	BLA = -0.09	4.400	3-8	This work
	Maximum ^a	6.091	3-8	This work
	BLA = -0.08	5.111	3-8	This work
	BLA = -0.07	5.969	3-8	This work
	BLA = -0.06	6.727	3-8	This work
	Minimum ^{a,d}	6.509	3-7	This work
	Computational Reference ²⁵	3.421	3-8	H-(CH=CH) _n -H, N = n using the 6-31G + PD basis set w. SOS
	Computational Reference ²⁶	4.004	3-8	H-(CH=CH) _n -H, N = n using AM1/FF

^aThat bond length alternation that maximizes/minimizes the quantity of interest. In the case of γ , the maxima refers to that for the least charge separated form (i.e. BLA < 0).

^bComputational results are for $\omega = 0$ (Sum-over-states [SOS]) or static perturbing field (Finite Field [FF]). Experimental results for β are by EFISH = electric field-induced second harmonic generation. Definition of N is consistent throughout and is different from that used by other authors. Two double bonds are counted for a benzene ring and an additional double bond is counted for the bond in the acceptor. ^cFor a curve containing only 3 points (N = 3,5,7), m = 3.281. ^dCurve fit is to $|\gamma_{\min}|$.

In conclusion, these results provide structure-property relationships for donor-acceptor polyenes, both as a function of molecular length and as a function of the ground-state polarization and resulting bond length alternation in the molecules. In particular, we predict that molecules with a significantly lower magnitude bond length alternation than is observed in polyenes and diphenyl-capped polyenes can have larger hyperpolarizabilities *as well as faster increases in hyperpolarizability with increasing chain length*. Thus, we suggest that cyanines with 0 Å of bond length alternation and donor-acceptor polymethines with roughly |0.07| Å of bond length alternation be considered for third-order NLO applications. Likewise, we suggest that donor-acceptor polymethines with roughly |0.05| Å of bond length alternation be considered for second-order electrooptic applications.

Description of the computation.

General

Geometry optimizations of **1** ($R = \text{Me}$, $n = 2-7$) were accomplished using the AM1 parameterization available in MOPAC 6.0.^{3, 4} Using a Z-matrix definition for the starting molecular geometries, the distances, angles and dihedral angles between external point charges of opposite signs, and between two of the point charges (positive Sparkles) and the molecule (nitrogen atom) were fixed. To accomplish this task the molecules were held planar during this procedure. Using a less convenient external point charge arrangement in which the point charges were placed in the molecular plane, it was shown that μ , α , β , and γ versus bond length alternation were basically unchanged when the least planar molecule, **1** ($n = 3$), was alternately held planar and permitted to become nonplanar during geometry optimization. Likewise these two arrangements of the external point charges around the molecule (e.g. point charges in the molecular plane versus point charges perpendicular to the molecular plane) made little difference in μ , α , β , and γ when these quantities were plotted versus bond length alternation. The detailed shape of the electric field will of course be dependent upon the arrangement of the external point charges (Figure 1). This point has been considered, and alternate arrangements of the point charges were employed. These included a) four charges in the molecular plane, b) eight charges arranged as dipoles perpendicular to the molecular plane, and c) four charges at different distances from the donor and acceptor to account for donors and acceptors of different relative strengths. For all of these different arrangements, and even when the potential stabilization at one side of the molecule was 3 times that of the other (corresponding to a much weaker donor than acceptor and vice versa) the behavior of μ , α , β , and γ were essentially unchanged, and, in most cases, curves were superimposable when viewed versus bond length alternation. Again, it is not our intention to simulate the effect of a particular solvent or other medium upon a molecule with any given

external point charge arrangement but rather to probe the electronic and geometric changes in the molecule, and its (hyper)polarizabilities as it becomes more polarized. In this case, these results merely indicate that the specific point charge arrangement used to polarize the molecule is not critical to observing these effects.

The point charges (Sparkles) were moved in steps from 40 Å to 4 Å from the ends of the molecule in the trajectory shown in Figure 1. The step increment became smaller as the point charges approached the molecule and the change in electric field with a change in distance became larger, beginning with an increment of 10 Å (40 Å, 30 Å, 20 Å), followed by an increment of 1 Å (15 Å through 8 Å), and ending with an increment of 0.2 Å (8 Å through 4 Å) for $n = 3-6$. For $n = 7$, this last increment was varied as little as 0.0002 Å (between 6.8820 Å and 6.8840 Å) in an effort to map out the region around $BLA = 0$ Å. Despite the use of this small increment, this region was not mapped out. BLA jumped from -0.013 Å (for a Sparkle distance of 6.8840 Å) to +0.015 Å (for a Sparkle distance of 6.8838 Å). Reasons for the existence of this "forbidden region" in molecules of this length (and longer, results not presented here) are under consideration but may be related to charge localization in infinite polyenes^{35, 36} and long cyanine molecules.^{37, 38}

At each fixed Sparkle distance, the geometry was optimized, and μ , α , β and γ were calculated in the presence of these point charges using the finite-field subroutine⁵ available in MOPAC 6.0 using an SCF convergence criterion (SCFCRT) of 10^{-20} a.u. as recommended by Kurtz.⁵ All of these quantities are vectors or tensors, and, in most cases, average values are reported. These average values are: $\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$; $\beta_{\mu} = (3/5) \cdot (\beta \cdot \mu / |\mu|)$ where $\beta \cdot \mu = \beta_x \mu_x + \beta_y \mu_y + \beta_z \mu_z$ and $\beta_i = \{\beta_{iii} + \beta_{ijj} + \beta_{ikk}\}$; and $\gamma = (1/5) \cdot [\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2.0 \cdot (\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})]$. All reported values are obtained from the energy equations⁵ (E4) in the finite field subroutine. Values obtained from the dipole equations⁵ (DIP) differ by less than 1% of the E4 values.

It is important to note that although two explicit fields are applied to the molecule, the point charge field and the electric field within the finite field calculation, these fields have distinctly different effects on the molecule. In particular, the first field is permitted to influence both its geometric and electronic structure. Thus, at the start of the finite field computation, the molecule is in a new equilibrium geometry and electronic configuration, within which the hyperpolarizabilities are then calculated (Figure 3). By varying the strength of the electric field employed in the finite field routine both numerical accuracy problems and electron configurational changes, observed for field strengths that are too small and large, respectively were avoided (see below). Using point charges to polarize the electrons without permitting the molecular geometry to change results in a finite field calculation of a molecule in a non-equilibrium, polarized, state.

Likewise, removal of the point charges after geometry optimization, but before the finite field procedure leaves nuclei in a position corresponding to a polarized molecule, but removes the potential that stabilizes the polarization. Both of the above procedures were performed; however, for each case, since the nuclei and the electrons were not in equilibrium configurations, much larger applied fields were needed to polarize the molecule, as compared to applying a field and allowing the geometry to optimize. These results suggested to us that both the applied electric field and the position of the nuclei make important contributions to the polarization response and that the most reasonable procedure was to account for both effects.

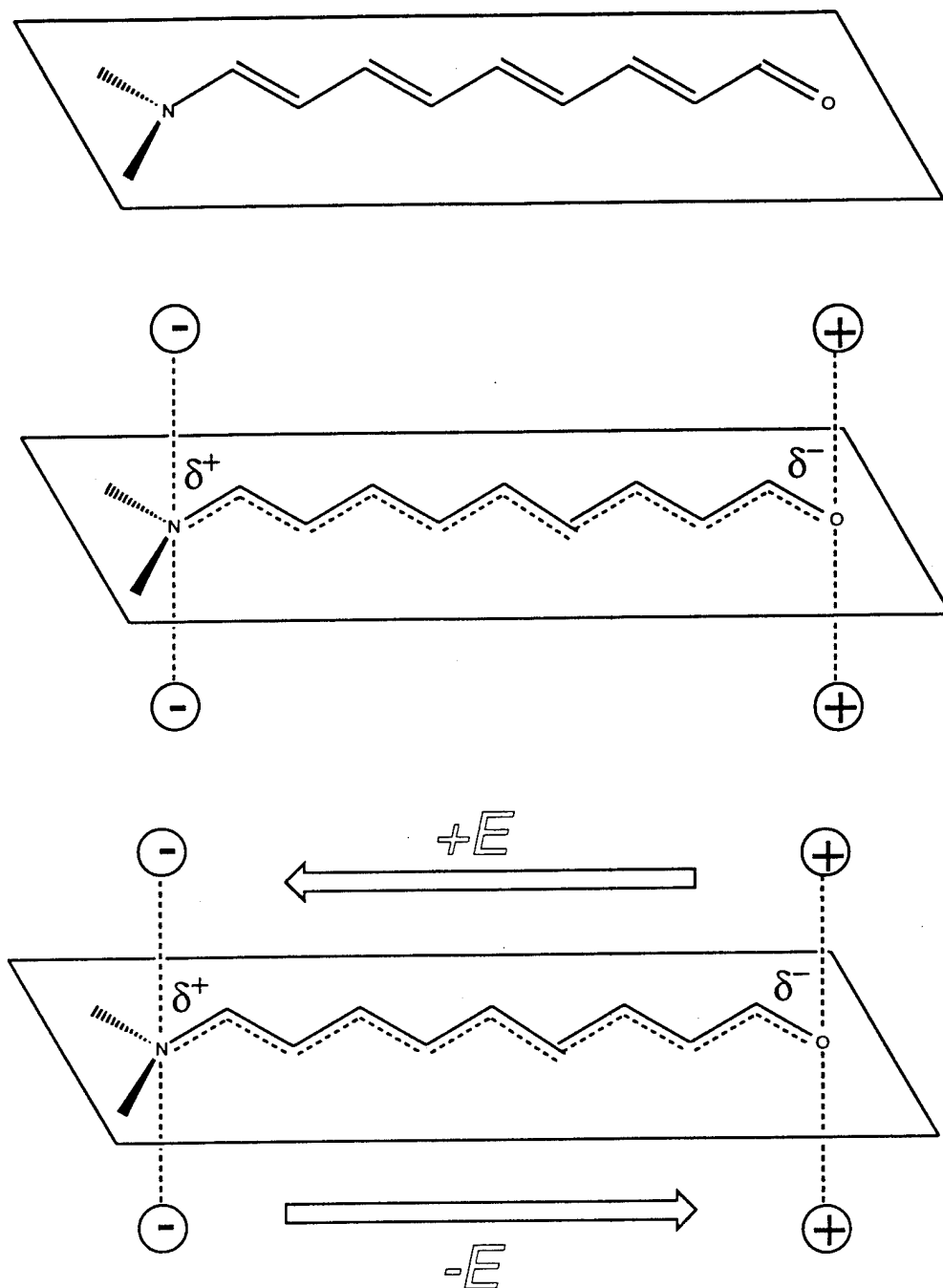


Figure 3. Molecule 1 [top] in the absence of an external electric field, [middle] exhibiting both nuclear and electronic polarization due to external point charges, and [bottom] exhibiting further electronic polarization (indicated by the arrows) as the result of the finite field procedure.

Tests of the finite field procedure

In the finite field procedure, the default strength of the perturbing electric field (10^{-3} a.u.) was employed, and all values reported are those obtained using this base field strength. To test

the validity of this field strength, it was varied to ensure that both numerical accuracy problems and electron configurational changes, observed for field strengths that are too small and large, respectively were avoided.⁵ Figure 4 shows the value of γ ($= (1/5) \cdot [\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2 \cdot (\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})]$) for 1 ($n = 4$) both in the presence and absence of the external point charges arranged as in Figure 1. This longer, more (hyper)polarizable molecule is much more sensitive to changes in applied field than were the smaller substituted benzenes reported earlier by Kurtz,⁵ indicating that this test is worth performing for these molecules. However, the external point charges do not significantly change the sensitivity of the computed (hyper)polarizabilities to the applied field. This observation is consistent with the conclusion that the molecule is in an equilibrium nuclear and electronic configuration at the start of the finite field procedure.

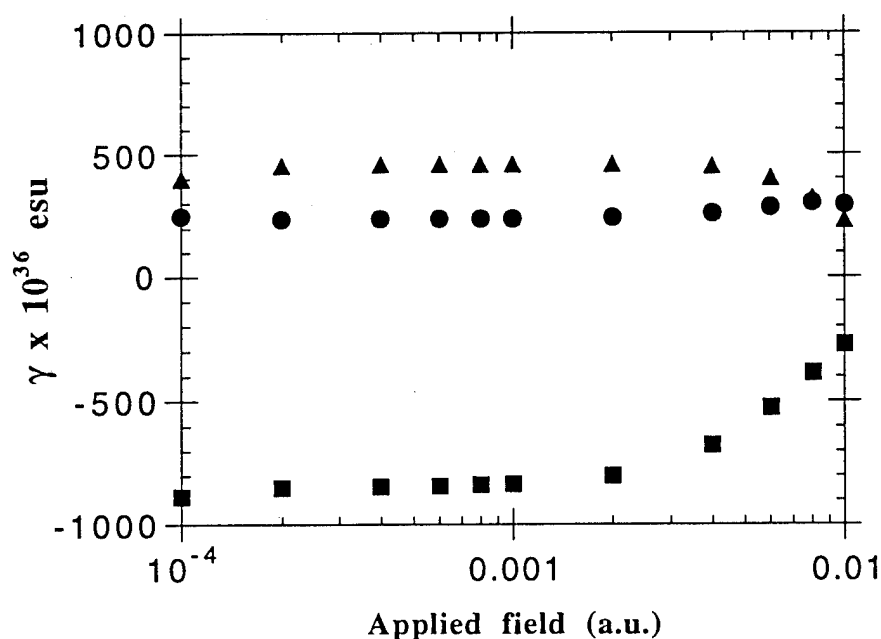


Figure 4. The sensitivity of γ (reported Figure 2), calculated using energy equations⁵ (E4) values from the finite field subroutine, for 1 with [circles] no point charges, [triangles] external point charges placed 10 Å from the molecule as in Figure 1 and [boxes] external point charges placed 6 Å from the molecule as in Figure 1. Over the range shown, the dipole equation values were comparable to those shown down to a field strength of 2×10^{-4} a.u. at which point they diverged.

Results at non-equilibrium configurations

Figure 5 shows β computed for **2** in what we rationalize as non-equilibrium configurations. In one case, (Figure 5, top) the molecule was geometry optimized in the gas phase and external point charges were placed around the molecule only for the finite field calculations, corresponding to a computation in a non-equilibrium configuration. The value of β increases as the molecule is polarized and even maximizes at approximately the same induced dipole moment as that observed when the geometry is permitted to optimize. The absence of nuclear relaxation, however, limits the extent of molecular polarization. In the second case, (Figure 5, bottom) the molecule was geometry optimized in the presence of the external point charges, and these were removed before the finite field calculation, corresponding to another non-equilibrium configuration. The molecule polarizes, as evidenced by an increase in dipole moment from 6 debye to > 30 debye over the range shown in the graph. This polarization again makes an incomplete contribution to the overall molecular polarization, evidenced by an even more sluggish response to the electric field applied in the first half of the procedure. Overall, it is our contention that both electronic and nuclear polarization make an important contribution to the configuration of the molecule, and both should be taken into account.

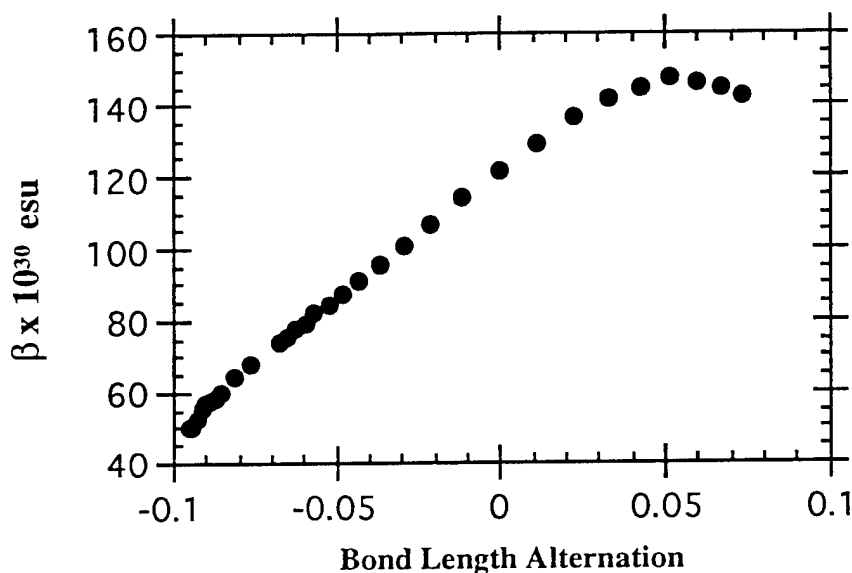


Figure 5. β calculated in two non-equilibrium scenarios for **2**. [Top] Plot of β versus μ where the molecule was geometry optimized in the gas phase and external point charges were placed around the molecule (as in Figure 1) only for the finite field calculations, corresponding to a computation in a non-equilibrium nuclear configuration. [Bottom] Plot of β versus bond length alternation the molecule was geometry optimized in the presence of the external point charges, and these were removed before the finite field calculation, corresponding to a non-equilibrium electronic configuration. β is plotted versus bond length alternation.

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The Effects of Aromaticity and Reduced Bond Length Alternation on Linear and Third-Order Polarizabilities of Conjugated Organic Chromophores

Introduction

The induced polarization of a molecule by an applied electric field, E , can be approximated by the power series expansion:

$$P_{\text{induced}} = \alpha_{ij}E + \beta_{ijk}/2 E \bullet E + \gamma_{ijkl}/6 E \bullet E \bullet E + \dots \quad (1)$$

Relationships between molecular structure and the linear polarizability (α), first hyperpolarizability (β) and second hyperpolarizability (γ) are of interest in the study of organic materials for nonlinear optics (NLO). In this paper, we employ a computational method (AM1 coupled with finite field) to examine these relationships for two classes of organic molecules: bipolaronic model compounds (organic dications/dianions) and cyanines (Figure 1). We rationalize the results of these computations by considering the effects of aromaticity, charge localization and bond length alternation upon the various molecules.

Procedure

Using the semi-empirical AM1 parameterization in the MOPAC package,^{1, 2} structures 1-5 (Figure 1) were geometry-optimized in the neutral (uncharged) form, in the dication form for 1, 3 and 4 and in the dianion form for 2 and 5. Cationic cyanine 6 was also geometry- optimized for different molecular lengths ($n = 2-10$). The geometry-optimization was not conducted with any defined symmetries, and for 1-5, molecular geometries were found to be mirror symmetric perpendicular to the long axis of the molecule within 0.01 Å. After geometry optimization, α and γ were calculated for all by a finite field subroutine.³ Average values for these tensors are reported, with $\alpha = (1/3) \cdot (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ and $\gamma = (1/5) \cdot [\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2.0 \cdot (\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})]$. Values reported (Table I) are those computed using the energy (E4) equations from MOPAC. Those computed using the dipole (DIP) equations differ by less than 2 % from the E4 values.

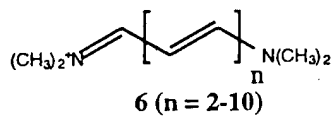
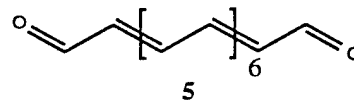
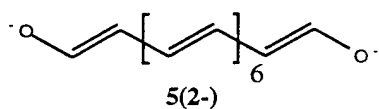
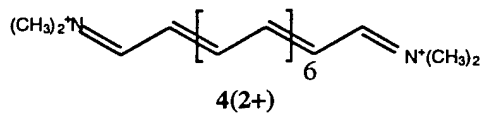
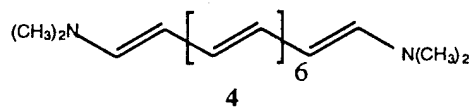
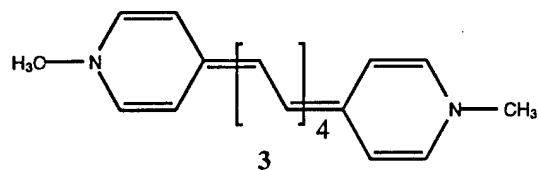
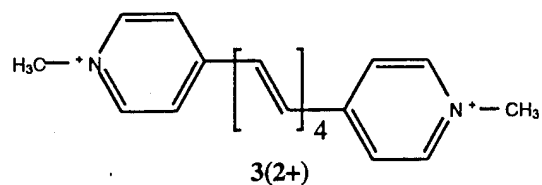
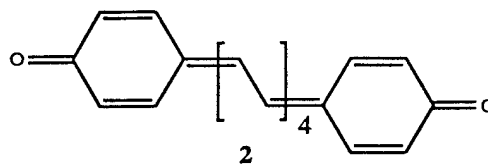
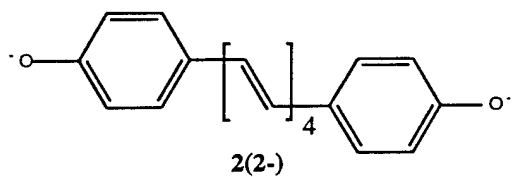
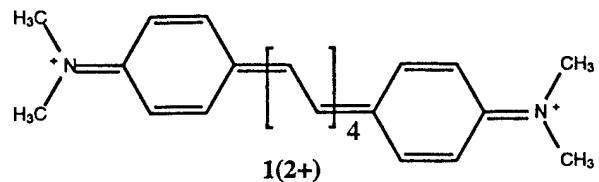
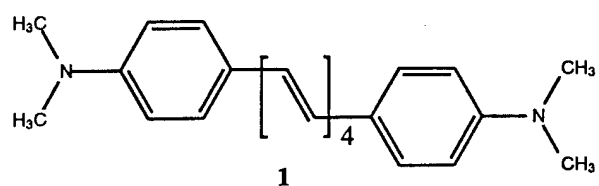


Figure 1. Molecules investigated in this study.

Table I. Linear (α) and third-order (γ) polarizabilities for 1-6.

<u>Neutral/Bipolaron</u>			<u>Cyanine (6)</u>		
	α^a	γ^b	n	α^a	γ^b
1	10.53	782.3	2	5.29	-124.9
1 (2+)	17.13	2595.0	3	8.51	-657.2
2 (2-)	11.89	1633.3	4	13.03	-2439.3
2	10.85	1070.9	5	18.87	-7207.0
3 (2+)	10.15	1120.5	6	26.41	-18295.9
3	11.69	1264.3	7	32.39	-14652.9
4	11.59	1354.3	8 ^c	28.34	30758.7
4 (2+)	15.32	3137.1	9 ^c	29.25	47736.9
5	8.55	726.6	10 ^c	28.65	44251.7
5 (2-)	14.84	1938.9			

^a $\times 10^{-23}$ esu; ^b $\times 10^{-36}$ esu; ^cCharge localization/bond length alternation observed -- see Figure 3.

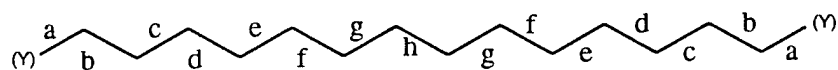
EFFECT OF OXIDATION/REDUCTION (BIPOLARON FORMATION) ON α and γ OF CONJUGATED ORGANICS

Increased γ has been predicted upon bipolaron formation (oxidation or reduction by two charges) for a number of conjugated organic systems, including polyene-derived chromophores.^{4, 5} We explore this hypothesis for compounds 1-5, and attempt to correlate changes in α and γ with concomitant changes in bond length alternation and aromaticity upon oxidation or reduction. Model compounds 1-5 are intended to represent synthetically accessible, discrete molecules that have different molecular topologies and that are sufficiently long to allow for significant charge separation.^{6, 7}

In our computations, polyene-based compounds 4 (upon oxidation) and 5 (upon reduction) display the predicted increases in α and γ . As expected, in the bipolarons, the charges build up near the ends of the molecules due to their mutual coulombic repulsion. Concurrently, bond length alternation (defined as the difference between the lengths of the single and double bonds, *where only non-ring bonds are considered, vide infra*) is reduced near the ends of the molecule (Table II), presumably due to partial delocalization of the charges. In longer systems, particularly conjugated polymers, further reduction in bond length alternation due to charge delocalization might be observed since the mutual coulombic repulsion may be greatly diminished

as the charges can separate and therefore delocalize over a greater distance. Properties such as the linear absorption spectra, solvatochromism, and linear and hyperpolarizabilities of organic chromophores are sensitive to changes in bond length alternation associated with the introduction of formal charges or increased charge separation.⁸⁻¹¹ Such effects have been discussed when comparing the optical spectra of polyenes, $R-(CH=CH)_n-R$, merocyanines, $R_2N-(CH=CH)_{n-1}-CH=O$ and cyanines, $R_2N-(CH=CH)_{n-1}-CH=NR_2^+$ of similar molecular lengths.⁸ Also, mid-gap (carrier) states in conjugated polymers formed upon doping (oxidation or reduction) alter their geometry, changing their electronic, and linear and non-linear optical properties.¹² Recently, enhanced γ has been observed in α,ω -diphenyl-octatetraene upon photoexcitation using a pump-probe experiment.¹³ Although the equilibrium geometry of this excited-state has not been determined, molecular orbital descriptions of related polyenes invoke reduced bond order alternation in the first allowed excited-state.^{14, 15}

Table II. Selected bond lengths (r , in Å, according to labelling scheme below) for the neutral/charged forms of **4** and **5**



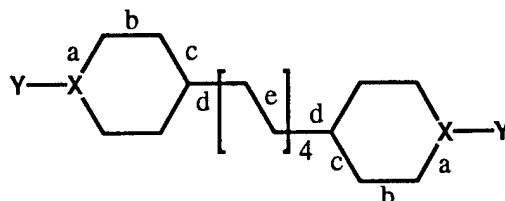
Y	Cmpd	a	b	c	d	e	f	g	h
$(CH_3)_2N$	4	1.39	1.36	1.44	1.35	1.44	1.35	1.44	1.35
$(CH_3)_2N^+$	4(2+)	1.33	1.43	1.37	1.43	1.36	1.44	1.35	1.45
O	5	1.23	1.47	1.34	1.45	1.35	1.44	1.35	1.44
O ⁻	5(2-)	1.26	1.41	1.39	1.38	1.42	1.36	1.43	1.35

In addition to effects arising from changes in bond length alternation, we find that the topology of a system containing aromatic/quinoidal rings is important. For example, when aromaticity increases upon oxidation (as with $\mathbf{3} \Rightarrow \mathbf{3(2+)}$), γ actually decreases. As indicated in Figure 1, **1**, **2**, and **3** were considered both in neutral and in charged forms. Resonance structures shown in Figure 1 approximately reflect the observed geometry-optimized structures. Selected bond lengths are shown in Table III.

In **1**, the molecule is aromatic in the uncharged state and becomes quinoidal upon oxidation. Its bond lengths suggest that the charges are localized near the ends of the molecule. The $N-C_{sp2}$ bond length decreases from 1.41 Å to 1.35 Å upon oxidation, consistent with increased bond order and assumption of positive charge by the nitrogen. Reduced bond length

alternation is observed immediately adjacent to the ring (bonds d and e, Table III) compared to that observed in the center of the chain ($r(\text{C}=\text{C}) = 1.35 \text{ \AA}$ and $r(\text{C}-\text{C}) = 1.44 \text{ \AA}$ for the central double and single bonds in **1(2+)**, respectively). Reduced aromaticity in the oxidized form is also expected to increase α and γ . In the aromatic form, the π -electrons are effectively delocalized within the rings; however, poor coupling between the rings and the adjacent polyene prevent effective delocalization into to the polyene.

Table III. Selected bond lengths (r , in \AA , according to labelling scheme below) for the neutral/charged forms of **1-3**



Y	X	Cmpd	a	b	c	d ^a	e ^b
(CH ₃) ₂ N	C	1	1.42	1.39	1.40	1.45	1.35
(CH ₃) ₂ N ⁺	C	1(2+)	1.45	1.36	1.44	1.37	1.43
O	C	2	1.47	1.34	1.46	1.36	1.44
O ⁻	C	2(2-)	1.45	1.37	1.41	1.43	1.35
CH ₃	N	3	1.39	1.36	1.45	1.36	1.44
CH ₃	N ⁺	3(2+)	1.37	1.39	1.41	1.44	1.35

^aFirst bond adjacent to ring; ^bSecond bond adjacent to ring.

Molecule **2** is quinoidal in the neutral state, but upon reduction, becomes more aromatic (Table III). The C-O bond ($r(\text{O}-\text{C}_{\text{sp}2})$) increases from 1.24 \AA to 1.26 \AA on reduction, consistent with a lowering of bond order suggested from the resonance structures in Figure 1. Furthermore, the center of the molecule displays the geometry expected from the aromatic form of **2(2-)** with the central single and double bond lengths of that form at 1.44 \AA and 1.35 \AA , respectively. Conversion to the aromatic form is not complete since, all of the negative charge would localize solely upon the oxygen atoms. Nevertheless, the expected decrease in α and γ due to the increase in aromaticity should partially offset increases in α or γ due to the two electron reduction. Correspondingly, much smaller increases in α and γ are predicted upon reduction of **2** than are predicted for **1** upon oxidation. The increase does, however, suggest that, for this molecule, the charges at the ends of the molecule and the decrease in bond length alternation are more important than the increase in aromaticity. When **3** is oxidized, its geometry distinctly changes from

quinoidal to aromatic (Table III) and both α and γ *decrease* (Table I). Thus, here, oxidation (bipolaron formation) increases both aromaticity and to a small extent bond length alternation, both of which appear to reduce α and γ .

In summary, for polyenes, **4** and **5**, bipolaron (charge) formation leads to enhanced α and γ . In the ring containing compounds there are two effects: the charge formation which may be expected to increase α and γ and a change from aromatic to quinoidal structures (or *vice versa*) concomitant with bipolaron formation. The electrons in the molecules with aromatic endgroups are expected to be less delocalized, resulting in a detrimental effect on γ . The molecular topology determines whether these two effects, charge formation and change in aromaticity are constructive or competitive. In **1**, upon oxidation, charges are formed and aromaticity is reduced; consequently, the largest increase in γ is predicted. In contrast for **2** and **3** the aromaticity increases upon charge formation, and the two effects cancel to a certain extent. Thus, in **2**, only a small increase in γ is predicted upon reduction, and in **3** γ is predicted to *decrease* upon oxidation. In conclusion, from these examples we suggest that it is not just the oxidation state (and charge) of a molecule but also its topology, degree of aromaticity and bond length alternation that influence α and γ .

CYANINES

The fact that cyanines exhibit very little bond length alternation can be rationalized by considering their two resonance structures (Figure 2). Since the two resonance forms are degenerate, each is expected to make an equal contribution to the description of the ground-state of the molecule, leading to no bond length alternation. Short chain length cyanines, such as **6** ($n = 2$ and **3**) have large negative γ values.¹⁶ Negative γ is found in other related molecules with degenerate resonance structures such as squarylium dyes.¹⁷

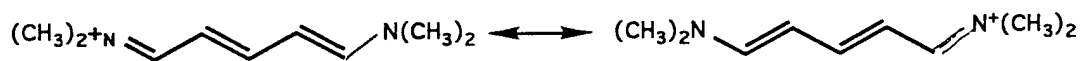


Figure 2. The two resonance forms contributing to the structure of **6**, shown for $n = 2$.

For short chain length cyanines, (**6**), our computations predict that γ is negative when n is small and increases in chain length, initially increase both α and $|\gamma|$. The correspondence between increased polarizabilities and increased molecular length is ubiquitous in NLO molecular structure-property studies. Interestingly, dramatic changes in α and γ occur when n increases from 6 to 7. The sign of γ changes, α decreases, and the bond length alternation (Figure 3) increases substantially. From the geometry, it appears that charge is localizing on one side of these longer molecules, indicating that the two resonance structures are contributing unequally to the ground-

state description of the molecule. The extent of charge delocalization in long conjugated systems has been considered for doped conjugated polymers¹⁸ and model compounds.¹⁹ Using other parameterizations available in MOPAC (MNDO, PM3), we observed increases in bond length alternation and corresponding changes in α and γ for **6** when $n = 6$ and 5 , respectively. Thus, this computation makes an interesting, specific prediction about the chain length at which cyanines will start to display charge localization and resulting increases in bond length alternation. The calculations suggest that, beyond this point, γ becomes increasingly positive, and for $n = 8$ it in fact changes sign. Certainly, the point at which these changes take place will be sensitive to the parameterization of the semi-empirical method and thus these results should be viewed with caution. Thus, it will be of interest to synthesize long cyanines and experimentally pursue this phenomenon as it suggests that the ultimate volume unit values for α and $|\gamma|$ is limited. Finally, we note that at comparable lengths, cyanines exhibit much large $|\gamma|$ than that of bipolarons. Thus, although **6** ($n = 7$) is one atom shorter than **4** ($2+$), $|\gamma|$ for the former compound is more than four times that of the latter.

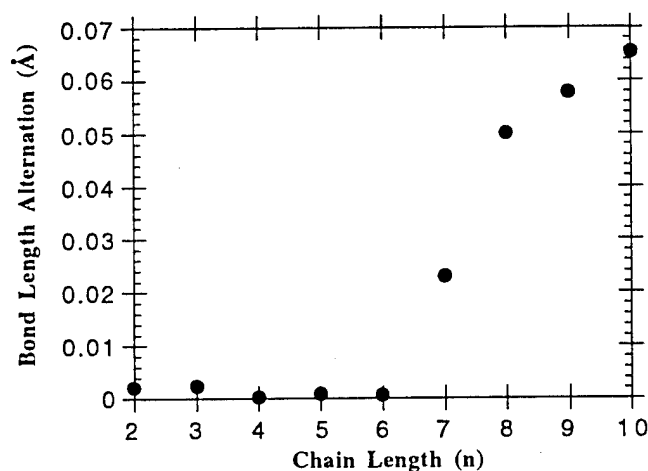


Figure 3. Bond length alternation (defined as the difference in the average of all $r(\text{C-C})$ distances minus the average of all $r(\text{C=C})$ distances in **6** for $n = 2-10$ (Figure 1)).

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c) Cumulative list of publications (With acknowledgment of funds from AFOSR grant or AASERT award):

1. Bourhill, G.; Mansour, K.; Tiemann, B.G.; Gorman, C.B.; Biddle, S.; Marder, S.R.; Perry, J.W. *"Third-Order Polarizabilities of Symmetric and Non-symmetric Polyene and Cyanine-Like Molecules."* Proc. SPIE, **1853**, 208 (1993).
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11. Bourhill, G.; Tiemann, B.G.; Perry, J.W.; Marder, S.R. *"The Effect of Ground-state Aromaticity on the Second Hyperpolarizability of Organic Donor -Acceptor Molecules."* Nonlinear Optics, submitted.

12. Meyers, F; Marder, S.R.; Pierce, B.M.; Brédas, J.-L. " *Tuning of Large Second Hyperpolarizabilities in Organic Compounds.*" Phys. Rev. Lett., submitted.
13. Marder S.R.; Cheng, L.-T.; Meyers, F.; Perry, J. W.; Bourhill, G.; Brédas, J.-L.; Pierce, B.; Cheng, L.-T. "A *Unified Description of Linear and Nonlinear Polarization in Organic Polymethine Dyes.*" Science, submitted.

d) List of Professional personnel associated with the research efforts:

Postdoctoral fellows who were supported either directly by salary or support for laboratory expenses are:

Peter Bedworth
Fabienne Meyers
Dennis Ng
Rafeal Ortiz
Chin-Ti Chen
Andrienne Friedli
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Dr. Joseph Perry (Jet Propulsion Laboratory)
Dr. Grant Bourhill (Jet Propulsion Laboratory)
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Dr. George Stegeman (Center for Research on Electrooptics and Lasers)
Dr. Jennifer Green (University of Oxford, England)

e). Interactions:

i) Papers presented at scientific conferences:

1. Bourhill, G.H.; Cheng, L.-T.; Gilmour, S.; Gorman, C.B.; Mansour, K.; Marder, S.R.; Perry, J.W.; Tiemann, B. G. "*Bond Alternation and Nonlinear Optical Properties of Organic Compounds.*" To be Presented at Progress in Nonlinear Optics: Organic and Polymeric Materials, Pullman, WA, July 16-17, 1992. (Invited Lecture).
2. Marder S.R.; Cheng, L.-T.; Gorman, C.B.; Murdoch, J.; Tiemann, B. G. "*Optimizing the Second-Order Optical Nonlinearities of Organic Molecules: Asymmetric cyanines and highly polarized polyenes.*" Presented at Society for Photooptical and Instrumentation Engineers National Meeting, San Diego, CA, July 20-25, 1992. (Invited Lecture).
3. Perry, J.W.; Marder, S.R.; Cheng, L.-T.; Bourhill, G.H.; Mansour, K.; Gorman, C.B.; Gilmour, S.; Tiemann, B. G. "*Nonlinear Polarizabilities of Symmetric and Non-symmetric Polyene and Cyanine-Like Molecules.*" Presented at Nonlinear Optics' 92: Optical Society of America National Meeting, Maui, HI, August 17-21, 1992.
4. Marder, S.R. "*Basic Design Strategies for Nonlinear Optical Materials.*" Presented at American Chemical Society National Meeting, Washington, DC, August 23-28, 1992. (Invited Lecture).
5. Marder, S.R.; Bourhill, G.H.; Cheng, L.-T.; Friedli, A.; Gilmour, S.; Gorman, C.B.; Mansour, K.; Perry, J.W.; Tiemann, B. G. "*The Relationship Between Bond Length Alternation and Nonlinear Hyperpolarizabilities.*" Presented at, The US- France Workshop on Optical Materials, Maubaisson, France, September, 28 - October 3, 1992. (Invited Paper).
6. Marder, S.R. "*A Chemist's View of Nonlinear Optical Materials.*" Presented at National Academy of Sciences Frontiers in Science Conference, Irvine, CA, November 5-7 1992. (Invited Lecture).
7. Marder, S.R. "*Optimizing the Nonlinear Optical Properties of Organic Materials.*" Presented at Ultrafine Particles in Glassy Matrices Conferences, Sponsored by Nippon Sheet Glass, Osaka, Japan, November 10-13, 1992. (Invited Lecture).
8. Gorman, C.B.; Marder, S. R. "*Theoretical Analysis of The Interrelationships of Linear Polarizability, First and Second Hyperpolarizability and Bond Length Alternation in Organic Donor-Acceptor Molecules.*" Presented at the Materials Research Society National Meeting, November 29- December 4, 1992.
9. Marder, S.R. "*Structure Property Relationships for Nonlinear Optical Properties of Hyperpolarizabilities.*" Presented at 5th Winter Conference of the Inter-American Photochemical Society, Clearwater Beach, FL, January, 2-6, 1993. (Invited Lecture).

10. Perry, J.W.; Marder, S.R.; Bourhill, G.H.; Mansour, K.; Gorman, C.B.; Tiemann, B. G. "*Third-Order Polarizabilities of Symmetric and Non-symmetric Polyene and Cyanine-Like Molecules.*" Presented at Organic and Biological Optoelectronics: Electro-Optics and Lasers Applications in Science and Engineering 93. Los Angeles, CA, January 16-23, 1993. (Invited Lecture).
11. Mansour, K.; Alvarez, D.; Perry, K.J.; Choong, I.; Marder, S.R.; Perry, J.W. "*Dynamics of Optical Limiting in Heavy-Atom Substituted Phthalocyanines.*" Presented at Organic and Biological Optoelectronics: Electro-Optics and Lasers Applications in Science and Engineering 93. Los Angeles, CA, January 16-23, 1993.
12. Mansour, K.; Alvarez, Jr., D.; Choong, I.; Perry, K.J.; Marder, S.R.; Perry, J.W. "*Nonlinear Absorption in Metallophthalocyanines.*" Presented at CLEO/QELS. Baltimore, MD, May 2-7, 1993.
13. Marder, S.R. "*Relationships Between Linear and Nonlinear Polarizabilities and Bond Length Alternation in Organic Molecules.*" Presented at the Canadian Chemical Society Nation Meeting, Sherbrooke, Quebec (Canada), May 30-June 4, 1993. (Invited Lecture).
14. Bourhill, G.H.; Brédas, J.L.; Cheng, L.-T.; Friedli, A.C.; Gorman, C. B.; Marder, S.R.; Meyers, F.; Perry, J.W.; Pierce, B.M.; Skindhøj, J.; Tiemann, B.G. "*Optimizing the First and Second Hyperpolarizabilities of Organic Dyes*" Presented at, Optical Society of America Topical Meeting: Organic Thin Films for Photonic Applications, Toronto, Canada, October 6-8, 1993. (Invited Lecture).
15. Marder, S.R. "*Attempts to Understand Relationships Between Chemical Structure and the Second- and Third-Order Optical Nonlinearities of Organic Molecules and Materials.*" Presented The First NSF-Sponsored Materials Chemistry Workshop, Albuquerque, NM, October 21-24, 1993.
16. Marder, S.R. ; Tiemann, B.G.; Perry, J.W.; Bourhill, G.H.; Gorman, C.B.; Friedli, A.C.; Cheng, L.-T.; Meyers, F.; Brédas, J.L.; Pierce, B.M. "*Structure Property Relationships for Second- and Third-Order Nonlinear Optics.*" Presented at Materials Research Society National Meeting, Boston, November 29 - December 3, 1993.(Invited Lecture).
17. Cheng, L.-T. Friedli, A.C.; Gilmour, S.; Gorman, C. B.; Marder, S. R.; Perry, J.W.; Perry, K. J.; Skindhøj, J.; Tiemann, B. G., Yang, E. "*The Effect of Bond Length Alternation on The Molecular Hyperpolarizabilities of Polymethine Dyes*" Presented at, The International Conference on Organic Nonlinear Optics, Val Thorens, (France) January 9-13, 1994.
18. Bourhill, G.H.; Cheng, L.-T.; Gorman, C. B.; Marder, S.R.; Perry, J.W.; Tiemann, B.G. "*Hyperpolarizabilities of Conjugated Donor-Acceptor Molecules with Varying Degree of Charge-Transfer in the Ground-State.*" Presented at, The International Conference on Organic Nonlinear Optics, Val Thorens, (France), January 9-13, 1994.

19. Marder, S.R. " *A Chemists View of the Science and Technology of Organic Nonlinear Optical Materials.* " To be presented at the American Chemical Society National Meeting, San Diego, CA, March 13-18, 1994.(Invited Lecture).
20. Marder, S. R. " *Designing Highly Nonlinear Organic Dyes* " To be presented at the Fourth Iketani Conference, The International Conference on Optical Nonlinear Organic Materials and Applications, Kona, HI May 17-20, 1994. (Invited Lecture).
21. Marder, S. R. " *The Relationship Between Ground-State Polarization and Molecular Polarizability and Hyperpolarizabilities of Organic Dyes* " To be presented at the Gordon Conference on Electronic Properties of the Organic Solid State, Andover, NH, July 24-29, 1994. (Invited Lecture).
22. Marder, S. R. " *Simple Model for Nonlinear Polarization in Organic Dyes* " To be presented at the Fifth Annual Symposium of the NSF Center for Photo-induced Charge Transfer, Rochester, NY August 1-3, 1994. (Invited Lecture).
23. Marder, S. R. " *Nonlinear Optical Properties of Organic Dyes* " To be presented at the Gordon Conference Electron Donor-Acceptor Interactions, Salve Regina, RI, August 14-19, 1994. (Invited Lecture)
24. Marder, S. R. " *Optimizing Molecular Hyperpolarizabilities in Linear Conjugated Organic Molecules* " To be presented at joint American Chemical Society, Optical Society of America Topical Meeting: Organic Thin Films for Photonic Applications, Washington DC, August 22-26, 1994. (Invited Lecture).
25. Marder, S. R. " *Nonlinear Optical Materials Design Criteria* " Presented at American Chemical Society National Meeting, Anaheim, CA, April, 1995. (Invited Lecture).
26. Marder, S. R. " *Rational Design of Nonlinear Optical Materials* " Presented by Fabienne Meyers at The Royal Society of Chemistry's Second International Meeting on Materials Chemistry, Kent, England, July, 18-21, 1995. (Plenary Lecture)

ii) none

f. none

g. none